An Initial Assessment of the Needs of the NSLS-II Molecular Environmental Sciences / Low-Temperature Geochemistry User Community

"NSLS-II User Workshop"
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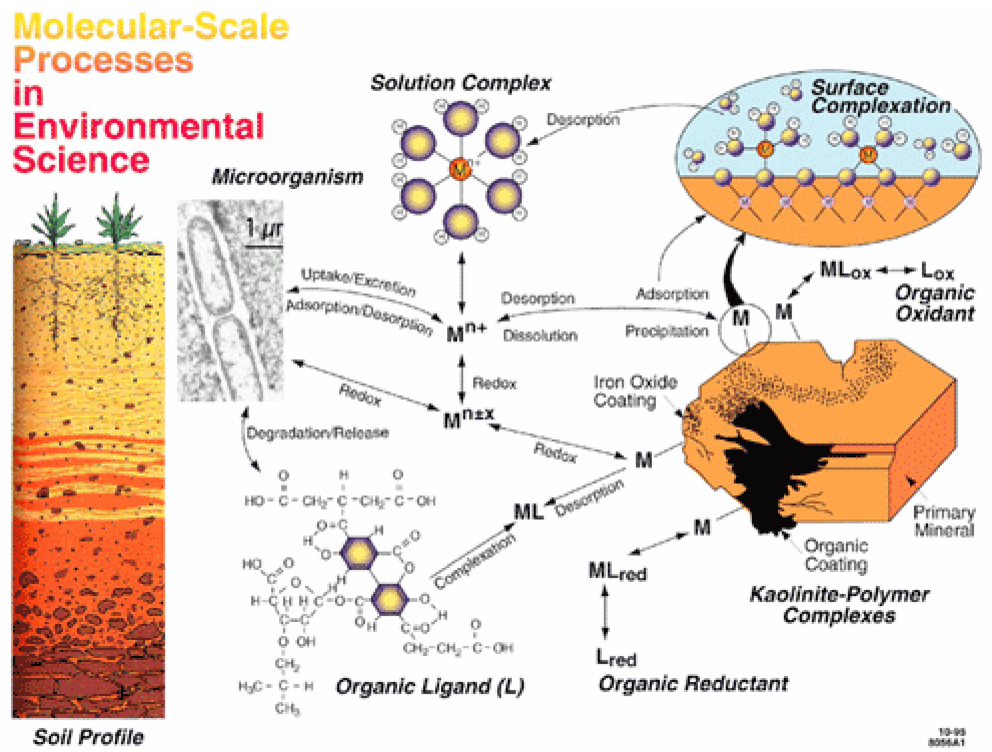

from Brown et al. (1999)

Contributors:
Antonio Lanzirotti – The University of Chicago
Jeffrey Fitts – Brookhaven National Laboratory
Chris Jacobsen - Stony Brook University
Paul Northrup – Brookhaven National Laboratory
John Parise – Stony Brook University
Bruce Ravel – Argonne National Laboratory
Rich Reeder – Stony Brook University
Steve Sutton – The University of Chicago

Introduction:
This report is an outgrowth of two workshops whose purpose in part was to address the opportunities that will be made available to the environmental sciences community as a result of the proposed NSLS-II facility. The first was a two-hour breakout session on environmental sciences held as part of the *"NSLS-II User Workshop"* at Brookhaven National Laboratory on July 17-18, 2007. This breakout session was attended by approximately thirty scientists with specific interests in environmental sciences research at the proposed NSLS-II facility. The second was the EnviroSync organized *"Workshop for Assessing the Synchrotron Radiation Needs of the Molecular Environmental Science (MES) and Low-temperature Geochemistry (LTG) Community"*, which was held on July 23-24, 2007, in Rockville, Maryland, and jointly sponsored by the Department of Energy (DOE) and the National Science Foundation (NSF). EnviroSync (www.environsync.org) is a grassroots organization established in 1998 to promote access to synchrotron radiation for scientists whose primary research is in the fields of molecular environmental sciences (MES) and low temperature geochemistry (LTG). Its members are leaders of North American research groups that use synchrotron radiation for such experiments in MES/LTG. The approximately 70 workshop participants represented a cross-section of researchers, program managers, and facility representatives. One of the outcomes of the EnviroSync workshop will be a report that will include community-wide recommendations for future developments at US synchrotron facilities that would benefit research in MES/LTG. The discussions that occurred at this workshop contained specific recommendations relating to beamline development at NSLS II in the context of broader community needs and we include relevant recommendations here to inform NSLS II leadership about the needs for the community.

We have structured this report to summarize 1) what some of the key scientific drivers for synchrotron based MES/LTG research are likely to be; 2) an evaluation of community growth and organization; 3) an overview of how this community utilizes synchrotron resources; and 4) recommendations for community needs at NSLS-II. We also summarize the beamline recommendations in tabulated form at the end of this report with estimates of beamline usage by the MES/LTG community. Our estimates suggest that about 8 MES/LTG equivalent beamlines are required, a number very similar to that currently used at the existing NSLS (Reeder et al., 2007).

Key Scientific Drivers for the MES/LTG Community:
Excerpting from the Executive Summary of the 2003 EnviroSync Molecular Environmental Science Report (Brown et al. 2003): "A major driving force for MES research is the need to characterize, treat, and/or dispose of vast quantities of contaminated materials, including groundwater, sediments, and soils, and to process wastes, at an estimated cost exceeding 150 billion dollars through 2070. A major component of this problem derives from high-level nuclear waste. Other significant components come from mining and industrial wastes, atmospheric pollutants derived from fossil fuel consumption, agricultural pesticides and fertilizers, and the pollution problems associated with animal waste run-off, all of which have major impacts on human health and welfare. Addressing these problems requires the development of new characterization and processing technologies – efforts that require information on the chemical speciation of heavy metals, radionuclides, and xenobiotic organic compounds and their reactions with environmental materials. To achieve this goal, both fundamental and targeted studies of complex environmental systems at a molecular level are needed…. MES SR studies have led to a revolution in our understanding of the fundamental physical and chemical aspects of natural systems."

Since the NSLS began operations in 1984, the MES/LTG community has vigorously utilized the resources available to them as molecular-level probes of the chemical and biological processes affecting the speciation and behavior of contaminants and pollutants in the biosphere (Fenter et al, 2002). Molecular scale studies of contaminant, nutrient, and molecular species involved in global cycling are required due to the natural heterogeneity and complexity of Earth and environmental materials. Soils, for example, are heterogeneous mixtures of crystalline, poorly crystalline or amorphous solid phases. These solid phases, in turn, may be coated by other micrometer or nanometer scale crystalline or amorphous phases, natural organic matter, fungi, or microbial biofilms. These surfaces are also invariably in contact with soil and atmospheric aqueous solutions and gases (Brown and Sturchio, 2002). Synchrotron-based X-ray and infrared techniques have emerged as very important tools for examining complex environmental samples to provide insights into the hydrobiogeochemical processes that control the fate, transport, and bioavailability of contaminants and nutrients. Synchrotron methods allow unique *in-situ* studies to be conducted at the spatial resolutions of interest with excellent detection sensitivity for minute contaminant abundances.

The complexity of such natural systems makes it unlikely that any single characterization method can provide all the information required about chemical speciation, spatial distribution, and physical associations needed to understand these processes and model them. The fundamental science driver for the community is arguably the need to make molecular level observations and scale them to the mesoscopic and macroscopic level required to model contaminant/nutrient behavior and design feasible remediation strategies. Thus, unlike many other communities that utilize synchrotron facilities, MES/LTG researchers utilize a variety of specialized beamlines and favor multi- and inter-disciplinary approaches. Synchrotron methods of particular interest to the community include x-ray absorption fine structure spectroscopy, x-ray microprobe, spectromicroscopy, microtomography, x-ray scattering, x-ray standing wave, and infrared spectroscopy.

The source characteristics of NSLS-II will allow this community to extend such studies to unprecedented scales, furthering insights into environmentally relevant molecular scale processes. Environmental science frequently involves the study of chemical speciation in natural materials that are heterogeneous down to the nanoscale. For example, studies of bioavailability and transport of metals and radionuclides in soils must contend with vastly different reactivity between clay particles, their organic coatings which may vary in thickness from nanometers to micrometers, and bacteria and their polysaccharide exudates, all in a hydrated environment. Spectroscopy of bulk samples, averaged over all of these different materials, is less likely to provide all of the information needed to identify the key, rate-limiting components. For this reason one can expect that more and more environmental science measurements such as spectroscopy and microdiffraction will be done as imaging experiments, experiments for which the NSLS-II source is clearly optimized. Some examples of the future scientific directions that this will enable include the following:

1. *Mineral interfacial reactions at the sub-grain scale.* Nanometer scale spatial resolutions that will be enabled by NSLS-II will enhance our ability to evaluate the reactivity, bioavailability, and toxicity of environmental particulates and species adsorbed onto particulate surfaces. Such studies applied to airborne particulates will have atmospheric implications for climate forcing models. For example what is the tendency for particulate types to be cloud condensation nuclii; are given groups of particles hydophobic or hydroscopic; how do their surface chemistry control aggregation and transport? Similarly, studies of colloids in natural systems are amenable to high resolution microspectroscopic analysis. Fundamental questions exist about whether such colloidal environmental particles form specific sizes of crystallites or aggregates. It's clear these will require study at the nanometer scale. Questions also exist about what controls the surface area of materials in surface and subsurface settings. This work will also extend to studies of colloids in marine settings and their impact on carbon cycling in the oceans. Such studies will have significant implications in modeling transport and partitioning of environmentally and energy relevant species through sediments, soils, and rock and on climate change model development.

2. *Biogeochemical processes at the nanometer scale*. There is a fundamental need to assess the micro- and nano-scale heterogeneity of metals and metalloids in biogeochemical cycles. NSLS-II will allow for complementary soft and hard x-ray imaging techniques that will let us investigate at the cellular level how organisms interact with contaminants in natural environments. For example, fundamental questions exist about the toxicity and biogeochemistry of manufactured and natural nanoparticles in the environment. Such studies will allow us to better define electron transfer mechanisms between microbes and minerals and image cell wall contaminant chemistry. Also of great importance is an improved understanding of the binding mechanisms of natural organic matter and bacteria. Such studies will also enable new scientific disciplines such as "environmental genomics". The opportunities to examine how genetic variations in organisms affect their interactions with contaminant and nutrient metal species in the environment is driven by the rapidly increasing amount of nucleotide sequence data that is becoming available. Such studies remain in their infancy, but synchrotron based x-ray techniques are extremely well suited to help evaluate how specific genes influence the uptake of metals in plants and animals and for imaging these interactions at the cellular level.

3. *Fluid flow and contaminant transport at the pore scale*. In modeling contaminant transport, there is a vital need to evaluate how grain boundary geometries in natural systems influence the

transport of chemical species in the subsurface. For example, perturbations on chemical migration may be much greater in fluids located in tight grain boundaries or within single mineral grains compared to fluids flowing through open cracks. Similarly, nanoscale confinement will alter the physiochemical properties of complex fluids and highly localized fluctuations in chemical conditions may occur due to leaching of mineral surfaces, nucleation and growth of new solids, and introduction of exotic elements from repositories (DOE, 2007). Advances in chemical imaging that will be made available by NSLS-II will offer excellent opportunities for imaging mineral-solution reactions in confined spaces *in-situ* within dense geologic media. Direct observations of pore scale transport may be possible, particularly in 3-dimensions using spatially resolved tomographic techniques. Since the average porosity of many subsurface lithologies has a natural size distribution at about 1 micron, the improvements in spatial resolution of x-ray micro- and nano- probes and for tomographic instruments will allow us to image and quantify the distribution of pore spaces, evaluate microbial distribution on pore walls, and micro-spectroscopically evaluate colloidal chemistry at mineral interfaces.

4. *In-situ and real time bulk x-ray diffraction of environmental materials*. In the 20th century, tools associated with room pressure and temperature (PT) bulk scattering techniques, coherent elastic and inelastic scattering from single crystals and powders for example, revolutionized our knowledge of the atomic arrangements and correlated vibrations in crystalline rock forming minerals. These static structure determinations, mostly based on the interpretation of the sharp Bragg diffraction from crystalline materials at room PT, provide the database of mineral structures often used as the starting point for the interpretation of spectroscopic data. Synchrotron X-rays allow us to push the boundaries of static studies to smaller samples for structure determination (µ-crystallography) and phase identification (µ-diffraction). As users push to ever greater resolution using XRF techniques, there will be an ever increasing need to correlate chemistry with phase (crystal structure). The high flux and brightness that will be available for scattering experiments at NSLS-II over a wide range of energies and employing optimized optics, detectors and sample environment allows us to conceive of experiments that open up whole new areas of research. These include real-time scattering to follow phase evolution as a function of time and environmental conditions (P, T, Eh, pH, fO_2 etc.). These techniques will allow us to mimic the conditions under which naturally occurring and engineered materials operate, and will provide results that allow us to compare engineered samples and environments with those found in nature.

5. *Crystallographically challenged environmental materials*: Determination of the atomic arrangements (speciation) in liquids and in other poorly crystalline (nano)materials is often considered to be the domain of X-ray absorption, since in these materials long-range periodicity is less important and the interatomic arrangement is dominated by short-range interactions. Studies of the total X-ray scattering (Bragg + diffuse component) provides correlations beyond, say, the second or third shell provided by XAS and it is these distances that are crucial to interpretation of the over-all atomic arrangement. In principle all atomic pair correlations out to the limit of structural coherence, nominally restricted by the cluster or particle size, are available by Fourier transforming the elastic total scattering to produce the Pair Distribution Function (PDF). The two techniques, XAS and PDF, are naturally complementary: XAS provides element specificity at environmentally realistic concentrations while the PDF is a rich data-set of interatomic distances that allows a more unambiguous derivation of atomic arrangement. Key to the continued development of the PDF technique for environmental investigation is the provision of bright high energy (E > 70 keV) X-ray sources, and excellent signal-to-noise discrimination over a wide dynamic range, since the diffuse elastic scattering is some 10^6 times weaker than typical Bragg scattering. High energies are capable of penetrating sample cells and provide data to high angle (Q), which is necessary to properly normalize the elastic component of the total scattering that will be Fourier transformed to obtain PDF. Beyond the range of structural coherence it is important to follow processes such as incipient precipitation, nano-particle nucleation, ripening and shape change as a function of processing under different environmental conditions. While wide-angle X-ray scattering (WAXS), say above Q=2 Å^{-1}, provides information about interatomic distances, modeling the small angle X-ray scattering (SAXS) provides information on particle size and

morphology. Both SAXS/WAXS measurements should ideally be performed simultaneously on the same sample contained in a controlled environment, in real time. While beamlines capable of such measurements are available none are optimized for the samples and sample environments likely to be of interest to the environmental scientist. Just as importantly, the researchers versed in these techniques are not environmental scientists and training opportunities for junior researchers in these areas are limited.

6. *Real-world x-ray absorption spectroscopy of environmental materials*: Bulk XAFS is -- and will remain -- a cornerstone of MES/LTG research. No other technique provides such versatile, non-destructive, element-specific access to local physical, chemical and electronic structure in complex matrices, in crystalline or noncrystalline materials, and *in-situ* under controlled environmental conditions. However, significant progress is still required in extending the capabilities of XAFS to allow for high resolution spectroscopy at real-world concentrations, abundances that are often below detection limits for current bulk XAFS techniques. A good example of this is mercury, which is a global environmental concern (and critical problem at some DOE sites). It is harmful in even low concentrations, accumulates in the food chain, and is governed by very complex and poorly-understood global atmospheric/terrestrial/marine cycling and molecular-scale transformation processes. The ability to study local speciation at realistic concentrations will greatly improve our understanding of these processes. The high flux and brightness of NSLS-II sources will provide unprecedented concentration sensitivity. XAFS studies of environmental samples also require analysis on various length scales, often in heterogeneous systems. The spatial resolution of XAFS measurements needs to be appropriate to the scale of the process being studied, and can vary from cm to mm, tens of microns (grain-scale), micron (cellular-scale), and nm (subcellular- and nanoparticle-scale). Thus a range of facilities (bulk, microprobe, nanoprobe) and versatility of focus are needed. NSLS-II will enable routine high-quality XAFS measurements over this wide range of spatial resolutions.

Evaluation of the NSLS/NSLS-II Environmental Sciences Community: Historically, the DOE synchrotron facilities have evaluated facility usage by environmental scientists by lumping them into the broad category of "Geosciences & Ecology". Certainly more accurate statistics could be garnered by updating these categories to more accurately reflect the research emphasis of the MES/LTG community, and the community encourages the facilities to do so. Existing statistics gathered by the NSLS facility since 1990 (Fig. 1) show that the percentage of users that are categorized as "Geosciences & Ecology" researchers at the NSLS have continued to grow at a rate of approximately 0.6% per year (with more rapid increases of about 1.5% per year since 2005). The community now constitutes about 14% of NSLS users, the third largest research group of the facility. Increases in subscription rates since 2005 have been largely driven by specific MES/LTG community initiatives jointly sponsored by DOE (BES and BER) and NSF beginning in 2003. These levels of subscription are consistent with statistics reported for this community from all four DOE operated synchrotron user facilities (EnviroSync Report 2007, *in prep.*) The community that has frequented the NSLS consists primarily of individual university and government agency principal investigators (PI's) funded through a variety of agencies supporting synchrotron based MES/LTG research. These agencies include DOE (primarily through the BES Geosciences Research Program and the BER Environmental Remediation Sciences Program), NSF (through the Divisions of Chemistry, Earth Sciences and Atmospheric Sciences, Geosciences Directorate),

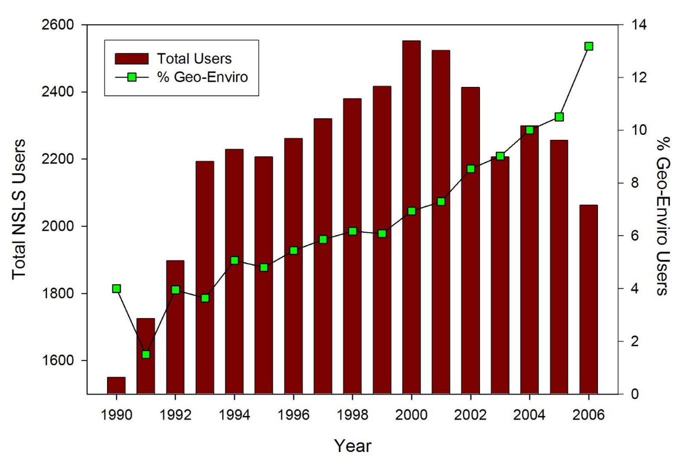

Figure 1. Graph of total NSLS Users (bar) compared to % of users in the Geoscience-Environmental Science field (1990-2006).

EPA (Office of Research and Development, Superfund, National Center For Environmental Research), and USDA (Agricultural Research Service). In addition to individual PI's, three "user groups" have played key roles in developing and supporting beamlines at the NSLS and to make them available to the broader environmental sciences community. These include:

- The University of Chicago's Center for Advanced Radiation Sources (CARS) – CARS is multi-institutional, multi-disciplinary consortium managed by the University of Chicago and tasked with developing synchrotron resources and expertise which are made available to the scientific community as National Synchrotron Resources for frontier research. At the NSLS, the hard x-ray microprobe X26A has been operated by CARS as such a facility (since 1989) dedicated to state-of-the-art research on earth materials and open to the entire scientific community through funding made available by DOE (BES-Geosciences Research Program, BER-ERSP).

- Stony Brook University Center for Molecular Environmental Sciences (CEMS) - CEMS is an Environmental Molecular Science Institute funded by NSF and DOE, with additional support from Stony Brook University and Brookhaven National Laboratory. Beginning in 2003, CEMS invested resources at the NSLS in support of the MES/LTG research community. These efforts included contributions in equipment and support to hard x-ray microprobe beamline X27A (built at the request of the MES/LTG community to accommodate heavy oversubscription on X26A), scanning transmission x-ray microprobe beamline X1A, and EXAFS beamline X11A.

- BNL Environmental Sciences Department – Primarily through resources made available to the department through DOE-BER's Environmental Remediation Sciences Program, the BNL Environmental Sciences Department moved forward in 2003 with an initiative referred to as EnviroSuite, a program designed to help support MES/LTG research at the NSLS. This initiative, in conjunction with the NSLS and CEMS helped develop a new hard x-ray microprobe at X27A to meet the demands of the MES community. In 2004 and 2005 EnviroSuite, subsequently assumed management of beamlines X15B (for low-energy

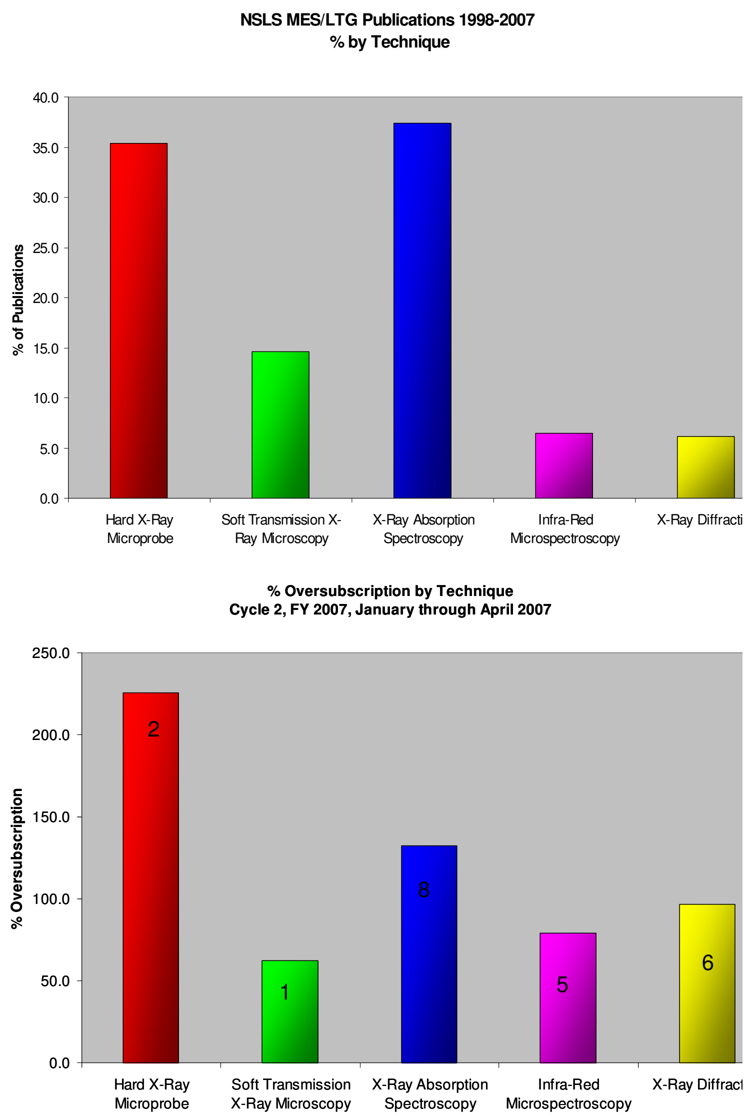

Figure 2. Top - % of NSLS MES/LTG publications by technique (1998-2007). Bottom - % oversubscription by technique (NSLS Cycle 2 , 2007) and number of BL's supporting the technique. HXRM, STXM, XAS, FTIR, XRD.

bulk XAS) and beamlines X11A/B (for high energy bulk XAS). EnviroSuite has also enhanced facilities and supported their operation by forming partnerships with universities, industry, and other agencies funded by NSF, DOE BES, USDA, NRL, etc.

Community Beamline Utilization:

The MES/LTG community utilizes a relatively broad spectrum of beamlines at 2nd and 3rd generation light sources. At the NSLS between 1998 and 2007 the majority of MES/LTG publications utilized beamlines specialized for (Fig. 2a) bulk x-ray absorption spectroscopy (37%), hard x-ray microprobe techniques (36%), scanning transmission x-ray microspectroscopy (15%), x-ray diffraction (6%), and infrared microspectroscopy (6%). The beamlines frequented by the community are also typically highly oversubscribed (Fig. 2b). For example, the two dedicated hard x-ray microprobes at the NSLS in cycle 2 of FY 2007 were oversubscribed by 226% overall. For x-ray absorption spectroscopy even with the availability of eight beamlines, the technique was oversubscribed by 132% for the same period. These five techniques are expected to remain the primary drivers for the next generation of MES/LTG experiments at NSLS-II. In addition to this suite of techniques, x-ray surface scattering techniques (such as X-ray reflectivity and grazing incidence X-ray scattering studies) have become more highly utilized by the community over the past several years at the Advanced Photon Source, and we expect they would be increasingly utilized by the MES/LTG community at NSLS-II.

Recommendations for NSLS-II:

Based on the input from the two workshops mentioned above, the following evaluation of MES/LTG needs at NSLS-II are provided subdivided by technique. These sections are accompanied by a table that summarizes these anticipated beamline needs including estimates for the minimum fraction of each beamline to be used by the MES/LTG community.

X-ray Absorption Fine Structure (XAFS)

Bulk XAFS is a core competence of the MES/LTG community and is a crucial tool to cutting edge MES/LTG science. A strong grounding in bulk EXAFS enables the excellent development of micro- and nano-beam spectroscopy methods for our community. There are currently 8 bulk XAFS beamlines at the NSLS, all on bending-magnet sources. Of these, 1.85 effective beamlines are used for MES/LTG experiments and overall subscription is 132%. Quick EXAFS is under development at X18B, and low-energy XAS for MES/LTG is currently conducted at X15B. The advanced capabilities of NSLS-II will open up new opportunities for continued and enhanced use of XAS in increasingly challenging materials. We recommend a “shared and optimized” approach to beamline involvement. Many MES/LTG applications of XAS share common requirements with those of other fields (e.g., life sciences and material science) and can be accomplished at beamlines supporting a range of capabilities, while a larger portion of MES/LTG work requires specialized beamlines and scientific staff optimized for this community.

1. *Source Requirements*: We estimate that at a bare minimum, the MES/LTG community will require the equivalent of a full three pole wiggler (TPW) and 80% of a soft bend for bulk spectroscopy. The TPW source will fill several niches that cannot be filled by the DW – including measurements of aqueous and biological samples that will not tolerate the photon flux of the DW source. Given that the DW source will require extensive filters to manage heat load, the minimum energy that could potentially be usefully utilized will be near the Ti K-edge. Consequently, the TPW beamlines will be relied upon to provide good flux down to 4 keV (i.e. the Ca edge). We expect the TPW and DW beamlines will be utilized heavily to their highest energies that maintain good flux. The soft bends will be relied upon for measurements up to about 4keV. All three XAS sources will need to deliver a large, stable beam suitable for the bulk components of all experiments. That said, all three sources will also need to provide a complimentary set of smaller spot sizes (while recognizing that the core XAFS experiments in MES/LTG are not driven directly to the smallest possible spot sizes). To offer an example, a study of a phytoremediative plant can use a 250 micron spot to examine metal distribution over whole-plant length scales, a 1-5 micron spot to examine the locations of metal accumulation, and a sub micron spot to examine metal distribution within an individual cell or vacuole.

2. *Heat Load Concerns*: It is also important to emphasize that while DW EXAFS will be vitally important for analyses requiring high flux and broad spectral range, environmental science materials are particularly sensitive to photo-induced changes in oxidation state and speciation. Heat load concerns will limit the ability of the DW to reach below the Ti edge and the high flux of the DW will preclude measurements on particularly radiation sensitive samples. For these reasons it is critical that the MES/LTG community also have access to XAFS resources developed on TPW sources. The XAFS beamlines will also benefit significantly from ring operation in top-off mode and we are confident that the beam stability requirements for the NSLS-II floor will meet any MES/LTG needs.

3. *QXAFS*: Time is critical for two types of applications in MES/LTG, those with time-sensitive samples and time-resolved studies of chemical/physical processes. Many MES samples are delicate and reactive combinations of solid, liquid, and organics. High flux and brightness, combined with appropriate detection, will be needed to collect high-quality XAFS data while minimizing time and exposure. Time-resolved “Quick XAFS” requires a dedicated beamline with specially designed rapid-motion monochromator and high-speed detection. Many important MES/LTG processes are ideal for QXAFS studies but their low concentrations present great challenges at currently-available facilities. The QXAFS capabilities of the existing X18B port at the NSLS continue to be developed and the community encourages this. With continued upgrades of QXAFS and detector capabilities, we feel it is likely that these components could be migrated from NSLS X18B to a focused 3-pole wiggler or an undulator source at NSLS-II.

4. *Energy Resolution*: Several elements of MES/LTG interest (e.g., P, Cr, Mn, Fe, As, U) can be characterized by very sharp XANES features and/or subtle shifts in their position. To fully utilize these features, and to employ combination fitting to quantify mixtures of known components, will require higher energy resolution than is typically available at current facilities (e.g. Si(111) monochromator with 10^{-4} resolution). The high flux and small divergence at NSLS-II will be ideal for producing higher-resolution (10^{-5} or better) monochromatic beams for these applications.

5. *Detector Development*: Higher photon flux and faster data collection modes require that detectors be able to process high total fluorescence count rates with corresponding high data read rates. Detector development is encouraged as part of the NSLS-II R&D efforts to ensure that experiments can take full advantage of source flux and brightness. Another problem often faced by studies involving low concentrations in a heterogeneous matrix, is having weak target signal amid high scattered and fluorescence backgrounds, and with interfering elements. This is exacerbated by higher flux, but can be remedied by employing energy-selective (WDS or equivalent) detectors.

Hard X-Ray Microprobe (HXRM)

There are two dedicated hard x-ray microprobe (HXRM) beamlines at NSLS, each with ~60% of available beam time used for MES/LTG research (a total of 1.2 effective beamlines). The HXRM beamlines are typically oversubscribed by a factor of 2-3X indicating that the demand is equivalent to 3 full time beamlines. Both currently employ Kirkpatrick-Baez microfocusing mirrors to achieve focused spots of 5-10 µm in diameter (FWHM), i.e., near the source size limit for NSLS, over the broad energy range required by this community (2-30 keV). Clearly there is a desire in the community to pursue continued improvements in microprobe spatial resolution and capabilities as a means of extending microfocused spectroscopies to the complex chemistry observed in natural systems at the molecular scale. However, at the same time, there will continue to be demand for more sensitive analyses with larger beams. Thus, the capability to trade-off spatial resolution and sensitivity is a high priority.

We recommend three parallel, microprobe development avenues for the MES/LTG community to realize this capability:

1. *Beamline Migration*: The existing two HXRMs at the NSLS should be migrated to NSLS-II in order to continue to serve the existing user community and provide them with enhanced capabilities. This migration process should include continued upgrade of optics and detectors of

each instrument. A particularly attractive transition plan has one of the HXRMs moving at an early stage to a 3-pole wiggler source at NSLS-II while the second continues to run at NSLS. Subsequently, the second HXRM would migrate to a U19 source, thereby minimizing the amount of reduced HXRM capacity. These two beamlines could be used nearly 100% of the time by the MES/LTG community. This plan will be relatively cost effective but will still leave the current HXRM demand underserved. The 3-pole wiggler source has a similar energy spectrum to the NSLS bend but with higher brightness. The U19 hard x-ray undulator will be an ideal microprobe source for experiments in the 1 to 10 keV range. Our calculations show that the current KB optics employed at the NSLS HXRM beamlines could achieve spatial resolutions of 600 nm on an NSLS-II three pole wiggler and 130 nm on the planned U19 hard x-ray undulator. With continued upgrades in optics, it is conceivable that these KB based beamlines could achieve spatial resolutions in the 10's of nanometers given the characteristics of the NSLS-II source. In addition, planned development of a lower-energy (1-5 keV) microprobe at NSLS X15B would serve applications which are highly desired but currently unsatisfied in the US. This microprobe would be very well suited to the soft bending magnet source at NSLS-II, and would be especially useful in conjunction with bulk XAS in the same energy range.

2. *EXAFS Beamline*: One of the initial six beamlines is for EXAFS utilizing a damping wiggler. This source will be valuable for microbeam experiments particularly at higher energy than the undulator and 3-pole wiggler can reach with usable brightness. We encourage this team to pursue their plans for a microbeam capability on this beamline and work to implement a canted ID geometry (one branch bulk, one microbeam) at the earliest opportunity. It will be crucial that the MES/LTG community participate in this beamline advisory team (BAT).

3. *Nanoprobe Program*: The spatial resolutions potentially achievable by the hard x-ray nanoprobe that is planned as part of the initial suite of six facility beamlines has great potential in opening new research directions in microspectroscopy for MES relevant materials. Given the known level of subscription by the MES/LTG community of such zone plate based microprobe beamlines nationally, we recommend that representatives of the MES/LTG community participate on the BAT for this beamline. We anticipate that this community will use at least 10% of the beam time on this beamline.

Special HXRM requirements include high source and optics stability for stable microbeam production, cryogenic sample stages and ancillary laboratory space and instruments for sample preparation. The HXRM runs best with the ring operated in top-off mode, i.e., fast timing experiments are currently rare. Both energy dispersive and wavelength dispersive fluorescence detectors along with 2D XRD detectors are needed for this work. Data acquisition and processing software development and standardization is important, particularly given the desirability of storing the entire collected energy dispersive spectra for each pixel analyzed and as the number of elements in array detector systems increases. These trends are rapidly increasing the size of acquired data sets and makes processing results in real time quite challenging.

<u>Scanning Transmission X-ray Microprobe (STXM)</u>
A molecular-level process understanding of key contaminant reactions (actinides and heavy metals/metalloids) in the environment requires us to examine contaminant adsorption/complexation and structural incorporation in mineral phases. The reactivity of structural components on these surfaces are typically sub micron in size and vary dramatically in composition, including both natural organics (e.g., humic acids and fulvic acids) and inorganic mineral phases (e.g., iron oxy-hydroxides and clays). STXM microspectroscopy techniques are invaluable in studying these small environmentally important materials and the source characteristics of NSLS-II will offer dramatic improvements in instrument brightness. At the recent the EnviroSync workshop, there was strong consensus on the future challenges for STXM spectromicroscopy. These include:

1. *Access to instruments and beamline migration*: Even with multiple soft x-ray STXMs in the US, about three times more beamtime is requested nationally than is available. New investigators must face the daunting prospect of waiting a year or more to get a few days of

beamtime, which makes it very difficult for them to incorporate synchrotron radiation techniques into their research. The existing X1A1 STXM instrument at the NSLS should be migrated to NSLS-II in order to continue to serve the existing user community and provide them with enhanced capabilities. This migration process should include continued upgrade of the X1A1 zone plate optics, detectors, and spherical grating.

2. *Improved spatial resolutions and broad energy ranges*: There is a strong desire to improve the spatial resolution towards a goal of 10 nm, which seems achievable but only with a long-term, well funded R&D effort on the fabrication of large-diameter zone plates. Nanofocusing optics for ~10 keV x-rays are part of the NSLS-II R&D plan, with an emphasis on multilayer Laue lenses which promise high resolution but which are not suited for use at lower energies or with easy energy tunability. The environmental sciences community strongly encourages efforts that have been proposed to complement NSLS-II R&D activities with the long-standing expertise of Stony Brook University in the development of higher resolution zone plate optics using the facilities of Brookhaven's Center for Functional Nanomaterials and the Joint Photon Science Institute. There is also a distinct need to be able to combine information gathered from the K edges of organic species organics and from the L edges of metals. This is best accomplished with on a STXM instrument with an energy range from 200 to perhaps 2,500 eV, ideally in a single instrument.

3. *Improved Detectors*: NSLS-II will make new demands on fluorescence detectors in terms of collection efficiency (so as to minimize radiation damage by collecting more of the signal) and count rate (because of the increased x-ray flux). In addition, phase-contrast detectors are required to put elemental concentrations into their ultrastructural context and to provide accurate concentration information. Robust, low-noise, high efficiency detectors are needed for both photon counting and current mode measurements in transmission. Detector segmentation has great potential in making phase contrast imaging possible. Incorporation of an incident flux monitor into the order sorting aperture used in STXM may be necessary for flux normalization; this will require significant R&D.

4. *Optimizing the sample environment*: Given the brightness of the NSLS-II source, radiation damage is a key concern, especially as spatial resolution is improved. For this reason it is essential to have at least one STXM with cryo capabilities. This is not a simple matter of putting a cooling stage on a sample mount, but rather a complete system with specimen transfer capabilities, tomographic tilt capabilities, and a low-mass stage to allow for rapid sample scanning. Additionally, since the MES/LTG community by the very nature of their science mission rarely employs a single synchrotron technique, there has been a long standing need from the community to have sample mounts that will allow for rapid sample migration from one beamline type to another. Compatible sample mounts either with fiducials on the mount, or fiducials on the sample substrate, are needed to allow one specimen to be studied with a variety of instruments (soft x-ray STXM, hard x-ray microprobe, infrared microspectroscopy). Analysis software must be developed that can merge the data from these various instruments and methods, so that one can overlay (in proper registration!) the full information obtained on the specimen.

Bulk Scattering and Environmental Science (BuSES)

We envision that BuSES applications will cover a wide energy range (7 – 120 keV), with anomalous scattering experiments at transition metal edges being conducted at ambient conditions at the low energy of the range and total scattering studies and/or work in gas pressure devices at the high end. To fully utilize these devices for time resolved experiments the community will also require new detectors with larger areas than are currently available, are faster (>1000 Hz), energy discriminating, express minimal dark current and have a large dynamic range (> 1000:1). Environmental chambers will also be required with capabilities for continuous control of temperature (from 0 K to 1300 K), humidity, fO_2, zeta eH, pH, and anaerobic/aerobic atmospheres. Further, the infrastructure to study radionuclides, collect small aliquots of effluent for flow-through experiments employing simultaneous HPLC or mass spec is needed. For the highest possible time resolution for solution speciation SAXS/WAXS, possibly with "pink" beams as well as mono and high band pass "white" beams are required.

Tying all these requirements together will require a strong software development effort in areas of data acquisition, analysis, simulation, and visualization. Interpretation of data with poor signal-to-noise discrimination will require integrated simulation along with representations of dynamical processes as 2D or 3D movies. Our ultimate aim is to develop a beamline acquisition and processing system that allows for ease of use by users and real time evaluation of data to improve the confidence level in data quality (as it is collected) and ultimately achieves higher productivity. We would also hope that all beamlines that conduct scattering experiments for this community use a common user interface and interchangeable sample cells.

Given the variety of programs, energy ranges and need to maximize flux the following are minimal requirements for the BuSES community:

1. One 3-pole wiggler for high resolution, ambient PT work.

2. Two damping wiggler beamlines, one dedicated to time resolved studies and one as a dedicated SAX/WAXS beamline.

3. One super conducting wiggler beamline for total scattering studies.

Infrared Microspectroscopy and Imaging

There is increasing demand by the MES/LTG community for the high resolution spectroscopic information retrievable for environmental samples using synchrotron based mid- and far-IR instruments. Because IR spectroscopy is especially sensitive to vibrations of O-H, C-H, C-O, N-H, and C-N bonds, it has great potential for applications to organic compounds and the chemistry of microbes, as well as for the identification of phases and of adsorbed organic species at specially designed mineral/water interfaces (Brown and Sturchio, 2002). Additionally, instruments optimized for far IR microspectroscopy can be used to constrain mineralogy in-situ and correlate this with the organic components present in the same sample. Coupled with microfocused x-ray techniques, unique information can be gathered of how speciation of heavy metal/metalloids species is modified by the presence of organic species in the environment. This will be facilitated by specifically designing IR sample mounts that can also be used at beamlines utilizing µXAS/ µEXAFS investigation techniques for environmental studies.

Presently on NSLS U10B, the MES/LTG community utilizes roughly 30% of the available time. We fully expect that this will be the minimum community demand at NSLS-II, but we suspect there is potential for the community to utilize up to 50% of the available time on similar instrument built on a soft bending magnet source at NSLS-II. Although we recognize that the flux and spatial resolution on these soft bend instruments will be comparable to what is currently available on the existing NSLS VUV-IR instruments, the exceptional requirements for beam stability at NSLS-II has the potential of increasing signal/noise of these instruments dramatically (~ a factor of up to 100x) for IR microspectroscopy applications, which will significantly improve detection sensitivity. The community also fully encourages the continued development of the array detectors for IR imaging studies. For the MES/LTG community, these instrumentation developments hold significant interest in improving our ability to image biofilms on grain surfaces. It is our understanding that coupled with high magnification objectives, the high signal/noise afforded by the stability of the NSLS-II source, and utilization of image oversampling techniques, there is an opportunity to improve spatial resolutions to the order of 1 micrometer.

Given the variety of programs the MES/LTG community utilizes in IR spectroscopy and imaging, the following are minimal requirements for the community at NSLS-II:

1. One mid- and far-IR confocal micro-spectroscopy instrument placed on a soft bending magnet source.

2. One mid-IR imaging instrument utilizing focal plane array detector systems and high resolution objectives.

We feel that continued upgrades of the U10B instrument should allow end station components to be effectively migrated to NSLS-II to continue to serve the MES/LTG user community. We also encourage continued instrumentation development in this regard.

Ancillary Laboratory Requirements:

MES/LTG users need a fully equipped geomicrobiology lab in close proximity to the beamlines. We also require a laboratory capable of handling radioactive samples. Other needs include an anoxic glove box, centrifuge, scales, pH meters, extensive wet chemistry equipment, table-top XRD, extensive sample prep equipment, a class-100 laminar flow hood, and both petrographic and low magnification microscopes. The microscope stations should ideally integrate CCD capture devices that are networked, so that images can be directly passed to beamline endstation computers. It would also be useful at some MES/LTG focused endstations to offer a large-volume anoxic sample environment (with gloves, load lock, and adequate volume to perform a wet chemistry experiment inside the chamber) in-line with the experiment. Other sample environment equipment will be needed as well (cryostat, furnace, sample change automation.) Many of these could potentially be made available in an XAS pool in conjunction with the other user communities. Ideally we would prefer to have these resources co-located within one LOB in the vicinity of MES/LTG focused beamlines.

Beamline Operations Staff

The MES/LTG community utilizes a wide variety of SR-based techniques. It will be crucial that members of the MES/LTG community participate intimately in BATs of beamlines that will be heavily utilized by this community. In addition, in our experience, users from this community benefit greatly from scientific collaborations with the beamline staff. This can be particularly beneficial when the beamline staff includes individuals with a background in molecular environmental science and/or earth science. The quality of publications is often greatly enhanced by such collaborations. Such collaborative environments are most readily developed by implementing beamlines dedicated to MES/LTG research, an approach that has been highly successful at many of the nation's SR facilities including the NSLS. We therefore recommend that the NSLS-II management seriously consider the development of MES/LTG dedicated beamlines or at a minimum include MES/LTG trained scientists in the operations teams of beamlines heavily utilized by this community.

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Optimal Suite of NSLS-II Beamlines to support the MES/LTG Science Mission

Beamline	Techniques	Est. % of Beam Time MES/LTG will Utilize	Optimal NSLS-II Source	Optimal Energy Range	Desired Monochromator	Desired Optics	Beam Size Goal (µm)	Desired Detectors
Microprobes								
1 - TPW HXRM	µXRF, µXAS, µXRD, fluorescence tomography	90	3-Pole Wiggler	2-20 keV	Si (111)/ Si (311)	KB Mirrors	< 0.2	solid state array detectors, EDS and WDS spectrometers, area detectors for µXRD
2 - U19 HXRM	µXRF, µXAS, µXRD, fluorescence tomography	90	U19 CMPU	2-25 keV	Si (111)/ Si (311)	KB Mirrors	< 0.05	solid state array detectors, EDS and WDS spectrometers, area detectors for µXRD
3 - EXAFS HXRM (project beamline)	µXAS, µXRF	20	DW100 Damping Wiggler	4-100 keV	Si (111)/ Si (311)	KB Mirrors	< 1	solid state array detectors; controlled sample environment
4 - Nanoprobe (project beamline)	µXRD, µXRF	10	U19 CMPU	hard X-rays		ML Laue	1 nm	solid state energy dispersive array detectors, diffractometer
5 – Low Energy XRM	µXAS, µXRF	80	Soft Bend Magnet	1-5 keV	Si(111)/others	macro focus plus KB Mirrors	< 0.25	solid state array detectors; helium sample environment
Bulk Scattering								
1 - TPW	high resolution, ambient PT scattering work	30	3-Pole Wiggler	2-20 keV	Highest E monochromatic possible	None or mirror	10-300	BNL strip/Multi-element analyzer array (>8 point detectors)
2 - DW-TR	time resolved scattering	30	DW100 Damping Wiggler	4-100 keV	Highest E/flux monochromatic possible	Removable mirrors	5 - 300	BNL strip/Area Detector
3 - DW-SAXS/WAXS	SAXS/WAXS	30	DW100 Damping Wiggler	4-100 keV	Highest E monochromatic possible	Removable Focusing optic	5 - 300	Area detector
4 - SCW	total scattering studies (PDF)	30	Superconducting Wiggler	4-100 keV	Highest E monochromatic possible	Removable CRO	2 - 500	Area detector
EXAFS								
1 - EXAFS (project beamline)	XANES, EXAFS, Grazing-incidence (µXAS listed above)	25	DW100 Damping Wiggler	4-100 keV	Si (111) etc., with high-energy-resolution mode available	horizontal focusing and horizontal collimation modes	1x1 to 5x40 mm	solid state array detectors, EDS and WDS spectrometers, detector for simultaneous powder XRD; controlled sample environment
2 - EXAFS-BM	XANES, EXAFS, Grazing-incidence	80	Soft Bend Magnet	1-5 keV	Beryl to Si(111)	macro focusing	1x1 mm	solid state array detectors, helium sample

	(µXAS listed above)							environment
3 - EXAFS-TPW	XANES, EXAFS, Grazing-incidence	90	3-Pole Wiggler	2-20 keV	Si(111)	macro focusing	1x1 mm	solid state array detectors
4 - QEXAFS-TPW	Quick XAS	20	3-Pole Wiggler	2-20 keV	Si(111)	macro focusing	1x1 mm	solid state array detectors, flow- and reaction-cells
STXM								
1 - STXM-SB	Scanning Transmission X-ray µSpectroscopy and Imaging, Diffraction Imaging	60	Soft Bend Magnet	100 eV-1 keV	spherical grating	zone plates or multi-layer Laue lenses	1-10 nm	Fluorescence detectors, phase contrast detectors
2 - STM-U19	Scanning Transmission X-ray µSpectroscopy and Imaging, Diffraction Imaging	60	U19 CMPU	100 eV-1 keV	spherical grating	zone plates or multi-layer laue Lenses	1-10 nm	Fluorescence detectors, phase contrast detectors
FTIR								
1 - IR-µSpec	mid- and far-IR microspectroscopy	50	Soft Bend Magnet	50-4000 cm^{-1}	interferometer		1-10 µm	Bolometer (far-IR), MCT-A (mid-IR)
2 - IR-imaging	mid-IR imaging	30	Soft Bend Magnet	500-4000 cm^{-1}	interferometer		1-10 µm	MCT-A FPA with a spectral range from 500-4000 cm-1

List of Attendees, Environmental Sciences Breakout Session, "NSLS-II User Workshop" at Brookhaven National Laboratory, July 17-18, 2007

Stephen Babalola, Brookhaven Nat. Laboratory
Gabriella Carini, Brookhaven Nat. Laboratory
Dev Chidambaram, Brookhaven Nat. Laboratory
Cleve Dodge, Brookhaven Nat. Laboratory
Jeffrey Fitts, Brookhaven Nat. Laboratory
Jon Friedrich, Fordham Univ.
Zugen Fu, Stony Brook University
Peter Genzer, CEGPA
Matt Ginder-Vogel, University of Delaware
Clare Grey, Stony Brook University
Quanzhong Guo, The University of Chicago
Albert Hanson, Brookhaven Nat. Laboratory
Ralph James, Brookhaven Nat. Laboratory
Keith Jones, Brookhaven Nat. Laboratory
Paul Kalb, Brookhaven Nat. Laboratory
Syed Khalid, Brookhaven Nat. Laboratory
Johnny Kirkland, Naval Research Laboratory
Antonio Lanzirotti, The University of Chicago
Wei Li, Stony Brook University
Lisa Miller, Brookhaven Nat. Laboratory
Satish Myneni, Princeton University
Paul Northrup, Brookhaven Nat. Laboratory
John Parise, Stony Brook University
William Rao, The University of Georgia
Bruce Ravel, Argonne Nat. Laboratory
Richard Reeder, Stony Brook University
Thorsten Schaefer, Research Center Karlsruhe
Jennifer Seiter, University of Delaware
Barry Siskind, BNL - NNSD
Randy Smith, Brookhaven Nat. Laboratory
Steve Sutton, The University of Chicago
Tetsu Tokunaga, Lawrence Berkeley Nat. Lab.
Glenn Werneburg, Stony Brook University
Creighton Wirick, Brookhaven Nat. Laboratory
James Yeck, Brookhaven Nat. Laboratory
Andrew Ying, Columbia University
Chet Zak, Minarik Corp.

List of Attendees, EnviroSync "Workshop for Assessing the Synchrotron Radiation Needs of the Molecular Environmental Science (MES) and Low-temperature Geochemistry (LTG) Community", July 23-24, 2007, Rockville, Maryland

Participants

John Bargar (Stanford University, SSRL)
Ben Bostick (Dartmouth)
Gordon Brown (Stanford University)
Peter Eng (University of Chicago)
Scott Fendorf (Stanford)
Paul Fenter (Argonne National Lab)
Jeffrey Fitts (Brookhaven National Laboratory)
Ben Gilbert (Lawrence Berkeley Nat. Lab)
Peter Heaney (Penn State)
Carol Hirschmugl (UW-Milwaukee, Aladdin)
Chris Jacobsen (Stony Brook University, NSLS)
Ken Kemner (Argonne National Laboratory, APS)
Antonio Lanzirotti (U. Chicago, NSLS)
Aaron Lindenberg (Stanford)
Satish Myneni (Princeton University)
Peter Nico (LBNL, ALS)
Paul Northrup (Brookhaven Nat. Lab, NSLS)
Peggy O'Day (UC Merced)
John Parise (Stony Brook University)
Bruce Ravel (ANL, APS)
Richard J. Reeder (Stony Brook University)
Amitava Roy (Lousiana State University, CAMD)
Kirk Scheckel (Environmental Protection Agency)
David Shuh (Lawrence Berkeley Nat. Lab, ALS)
Lynne Soderholm (Argonne National Lab, APS)
Donald Sparks (University of Delaware)
Neil Sturchio (U. Illinois-Chicago)
Steve Sutton (University of Chicago)
Glenn Waychunas (Lawrence Berkeley Nat. Lab)
Sam Webb (SSRL)

Funding Agency Program Managers

Todd Anderson (BER-DOE)
Paul Bayer (BER-DOE)
Marsha Bollinger (BES-DOE)
Patrick Dobson (BES-DOE)
Roland Hirsch (BER-DOE)
David Lambert (GEO-NSF)
Nick Woodward (BES-DOE)

Synchrotron Facility Representatives

Steve Dierker (Director, NSLS II)
David Ederer (CAMD)
Ernie Fontes (CHESS)
Mike Martin (ALS)
Lisa Miller (NSLS)
Dennis Mills (Deputy Director, APS)
Joachim Stöhr (Director, SSRL)